AFCRL-68-0189



# HIGH ENERGY MOLECULAR BEAMS

James B. Anderson and John B. Fenn

Princeton University
Princeton, New Jersey 08540

Contract No. AF19(628)-3887

Project No. 4076, 8658
Task No. 407604, 865802
Work Unit No. 86580201

FINAL REPORT

Period Covered: 1 March 1964 through 31 August 1967

January 1968

Contract Monitor: Farid Hushfar
Optical Physics Laboratory.



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## ABSTRACT

A description of research on producing high energy molecular beams under Contract AF 19(628)-3887 is given. Results of previously published work are summarized for the development of techniques for generating neutral beams in the 1 to 10 eV range using gas dynamic acceleration of heavy species by light carrier gases in nozzle flows from which molecular beams are extracted. Measurements of heavy species velocities, velocity distributions and intensities in the molecular beams formed are discussed in relation to theoretical predictions. Studies of the gas dynamics of free jets of pure gases and mixtures used as molecular beam sources are reported. A brief assessment of applications to research on atomic and molecular collision processes is included.

# INTRODUCTION

Molecular beam scattering experiments can in principle provide a detailed knowledge of atomic and molecular collision processes. One of the main reasons our knowledge of these processes is limited is that molecular beams with useful intensities have not been available in the energy range between 0.5 and 20 eV. Classical effusive or oven source beams have a useful upper limit to energy of about 0.5 eV while beams formed by charge exchange neutralization of ion beams are severely limited in intensity at energies below 100 eV. Collisions in the excluded energy range are responsible for many phenomena of interest and importance in chemical reaction, electronic excitation and molecular transport.

The objective of the research on this contract was the development of principles and techniques for achieving beams of neutral molecules at high intensities having energies in the range of one to ten electron volts. Research was particularly directed toward developing beams of nitrogen molecules in that energy range for bombarding target carbon dioxide molecules in studies of excitation of internal energy states. The general approach used was that of accelerating heavy molecules in a mixture with a light carrier gas during expansion through a

nozzle to form a supersonic jet from which a collimated molecular beam could be extracted. The research has resulted in the successful development of this approach into the "seeded-beam" technique. Using the technique a variety of molecules have been accelerated in mixtures with helium and hydrogen to produce molecular beams with energies well above one electron volt at intensities of $10^{16}$ to $10^{17}$ molecules per steradian-second.

The development of the means for producing high energy beams using gas mixtures has of necessity required investigation of the formation of lower energy beams by expansion of pure gases. Experimental and theoretical work in the gas dynamics of the free jet expansion has provided the understanding necessary for development and design of seeded-beam systems. Other phenomena associated with free jets and molecular beam formation have been investigated in detail. These include the interaction of free jets with background gas and collimators, the rotational relaxation of nitrogen in free jets and the diffusive separation of gas mixtures under the high pressure gradients of free jets.

The results of research carried out under the contract have been reported in detail in journal articles and conference proceedings. These are listed in a subsequent section of this report. We have recently reviewed the state-of-the-art of producing

molecular beams of neutral molecules in the range of one to twenty electron volts by various means (8) and by the use of supersonic jet sources (10). In this report we summarize the results of the research which has been carried out in our laboratory.

## SUMMARY AND ANALYSIS OF RESEARCH RESULTS

The nozzle source molecular beam techniques currently in use are derived from a proposal of Kantrowitz and Grey (12) in 1951 in which it was shown that advantages in beam intensities and velocity distributions might result if the conventional oven source for molecular beams were replaced by a low density supersonic gas jet. Within a few years these advantages were verified by experiments in several laboratories. In practice it was shown most convenient to use as sources free jets formed by expansion of gases from simple converging nozzles or orifices. The free jet has the advantage of avoiding problems of boundary layer formation in the diverging section of a nozzle and simplifies, to some extent, the gas dynamics of jet formations.

One of our early experiments on examining the characteristics of free jets and the beam formation process is that reported in Ref. (1). In this study the velocity distributions in molecular beams of argon from free jet sources were measured using a time-of-flight method. It was shown that the transition from continuum to free molecular flow in a free jet expansion results in

a "freezing" of axial molecular velocities and limits the minimum width of the velocity distribution which may be obtained. A translational temperature relaxation theory was successful in correlating the results. An improved model (which takes into account the transition to free molecular flow in the jet) for predicting beam intensities also resulted from this study. Further studies of velocity distributions obtained in free jets of pure gases were reported in Refs. (3) and (5).

The interaction of the jet with the skimmer or first collimating orifice in the beam formation system has been examined in several laboratories. Ideally, a skimmer would pass a central streamline of the jet into the main beam chamber without any alteration of molecular trajectories or velocities. For high jet densities this is not the case and maximum beam intensity is limited by "skimmer interference" with the flow. In Ref. (3) we reported the results of experiments with a cryogen-cooled skimmer designed to condense jet molecules on the skimmer surfaces and prevent their reflection and interference with jet molecules. We concluded that the decrease in the efficiency of beam formation at high jet densities was the direct result of reflection of molecules from skimmer surfaces and not due to self-scattering of beam molecules. Our interpretation of the results obtained in various laboratories is given in Ref. (10).

The pumping requirements for nozzle beam systems may in certain circumstances be considerably greater than for oven

beam systems. In Ref. (2) we reported studies of the interaction of background gas with free jets in the beam formation process. We observed that the free jet in effect behaves as a pump in clearing background gas from its central core. It was found that as an approximation the distance cleared by the jet is proportional to the nozzle flow rate and that further downstream simple scattering by background gas occurs. These results make possible much more accurate determination of pumping requirements for nozzle beam systems.

The low static temperatures reached in expansion of a jet may result in the gas becoming supersaturated and give rise to condensation. Since even dimer formation may interfere in many beam experiments, we made a theoretical study of the condensation process and developed a simple approximate theory of dimer formation which is in fair agreement with measurements in other laboratories. The results of our study were given in Ref. (3).

When a pure gas expands isentropically in a free jet, the average kinetic energy of the molecules is given by

$$\tfrac{1}{2}\, mV^2 = \int_{T}^{To} C_p dT \qquad (1)$$

where V is the flow velocity, m is the molecular mass, $C_p$ is the molecular specific heat at constant pressure, To is the stagnation

or source temperature, and T is the static temperature in the jet. At Mach numbers above 5 the static temperature in the jet approaches zero and the average kinetic energy approaches a limiting value -- about 0.05 eV for a room temperature source and 0.5 eV for a source at 3000°K. For a binary gas mixture of light and heavy molecules, if there are enough collisions to give temperature and velocity equilibration between species, the kinetic energy of the heavy molecules is given by

$$\tfrac{1}{2}\, MhV^2 = \frac{Mh}{Mm} \int_o^{To} CpmdT \qquad (2)$$

where the subscript m indicates the mean value for the mixture and h indicates the heavy species. For mixtures with a trace of heavy species the kinetic energy of the heavy species is higher than that of a pure gas by a factor approximately equal to the ratio of the masses of the heavy and light species. For a dilute mixture of argon in helium with a source temperature of 3000°K the argon kinetic energy would then be about 5 eV.

Using the time-of-flight technique to measure beam velocities and therefore the translational kinetic energies, we demonstrated experimentally that the gas dynamic acceleration of heavy species in a number of mixtures follows theoretical predictions. These experiments were reported in preliminary form in Ref. (4) and in more complete detail in Ref. (6). Results for various gas mixtures comprising one mole percent of heavy species in hydrogen and

helium at source temperatures of 300° to 2050°K are reproduced in Table I. For these data nozzle pressures were in the range of 100 to 300 torr with a 0.51 mm nozzle diameter. Theoretical velocities listed in the table were computed from Eq. (2) with the assumption that the heavy gas made no contribution to specific heat by the solute except for its translational energy.

In most cases the observed velocities are very close to the theoretical values. The departures become significant only for the very heavy species. We found that such departures can be overcome by increasing source density. The important feature of the results in Table I is the fact that the solute kinetic energies go well into the energy range above 0.5 ev. The highest values are realized, of course, with the highest source temperatures and with the heaviest species.

At low values of the source density (or Reynolds number) velocity equilibration between light and heavy species during the jet expansion is not complete and the energies predicted by Eq. (2) are not attained. This phenomenon can be accounted for quantitatively in terms of an axial pressure diffusion effect in the early stages of gas expansion. Both theoretical and experimental studies of this velocity "slip" between species were reported in Refs. (5) and (7).

Measurements of beam intensities obtained with the seeded beam tehcnique were made using an ion gauge manometer. Results were only approximate but the intensities of the heavy species were about those predicted by theory. Intensities of $10^{16}$ to $10^{17}$ molecules per steradian-second were measured. Several effects tend to concentrate the heavier molecules on the beam axis. The effect of radial pressure diffusion in the free jets was found to conform to predictions of a nearly-inviscid-flow theory. Measurements of the spatial distributions of species flux in free jets of gas mixtures were reported in Ref. (9). A second concentrating effect is that resulting from lower transverse velocities of the heavy species aft of the first collimator or skimmer.

Measurements of velocity distributions in beams formed from mixtures of helium and argon were reported in Ref. (5). Theoretical predictions of velocity distributions under similar conditions were given later in Ref. (7). Both theory and experiment indicate that temperature equilibration of the light and heavy species is not complete even if velocity equilibration is essentially complete. There is, however, a disparity between the measured and predicted heavy species velocity distributions which remains unresolved.

## RELATIONSHIP OF RESULTS TO CONTRACT OBJECTIVES

Principles and techniques for achieving beams of neutral molecules have been developed in accordance with stated contract objectives. The general approach of using a light gas to accelerate heavy molecules in the "seeded-beam" technique has been demonstrated to be successful for a variety of species including nitrogen molecules in the energy range of one to ten electron volts.

## IMPLICATIONS ON FUTURE WORK

The "seeded-beam" technique is now sufficiently developed for use in a number of experimental studies of atomic and molecular collision processes. The technique has been successfully used in our laboratory in measurements of momentum transfer at surfaces with argon beams at energies up to 4.11 eV (11) and in determinations of argon-argon total scattering cross-sections at collision energies up to 1.6 eV (13). Further investigation of the gas dynamic acceleration process is necessary prior to its use in many future experiments and a number of problems remain to be overcome. Nevertheless, in its current state the technique provides a valuable tool for research in collision processes and we expect it will continue to be used with success in an increasing variety of experiments.

## PREVIOUS PUBLICATIONS RESULTING FROM TOTAL OR PARTIAL SPONSORSHIP BY THE CONTRACT


1. "Velocity Distributions in Molecular Beams from Nozzle Sources". J. B. Anderson and J. B. Fenn, Physics of Fluids 8, 780 (1965).

2. "Background and Sampling Effects in Free Jet Studies by Molecular Beam Measurements", J. B. Fenn and J. B. Anderson, in Rarefied Gas Dynamics, Vol. 2 (Fourth Symposium, Toronto, 1964), pp. 311-330, Academic Press, New York, 1966.

3. "Studies of Low Density Supersonic Jets", J. B. Anderson, R. P. Andres, J. B. Fenn and G. Maise, ibid, pp. 106-127.

4. "Supersonic Nozzle Beams - Some Recent Experimental Results", N. Abuaf, J. B. Anderson, R. P. Andres, and J. B. Fenn, in Recent Advances in Aerothermochemistry, Vol. I (7th AGARD Colloquium, Oslo, 1966), pp. 339-361, AGARD CP No. 12, 1967.

5. "Studies of Low Density Supersonic Jets", N. Abuaf, J. B. Anderson, R. P. Andres, J. B. Fenn and D. R. Miller, in Rarefied Gas Dynamics, Vol. 2 (Fifth Symposium, Oxford, 1966), pp. 1317-1336, Academic Press, New York, 1966.

6. "Molecular Beams with Energies above One Electron Volt", N. Abuaf, J. B. Anderson, R. P. Andres, J. B. Fenn and D. R. Miller, Science 155, 997 (1967).

7. "Intermediate Energy Molecular Beams from Free Jets of Mixed Gases", J. B. Anderson, in Proceedings of the First International Symposium on Molecular Beams of High and Intermediate Energies (Cannes, 1967), in press.

8. "Molecular Beam Engineering at Intermediate Energies", J. B. Fenn, ibid., in press.

9. "Separation of Gas Mixtures in Free Jets", J. B. Anderson, A.I.Ch.E. Journal 13, 1188 (1967).

10. "New Methods for Producing High Energy Molecular Beams," in Proceedings of the 30th AGARD Propulsion and Energetics Panel Meeting (Munich, 1967), in press.

11. N. Abuaf and D. G. H. Marsden, in Rarefied Gas Dynamics, Vol. 1 (Fifth Symposium, Oxford, 1966), pp. 199-210, Academic Press, New York, 1966.

OTHER REFERENCES

12. A. Kantrowitz and J. Grey, Rev. Sci. Instr. 22, 328 (1951).

13. B. Baratz, Doctoral Thesis, Princeton University, 1967.

## CONTRIBUTORS TO RESEARCH REPORTED

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Nesim Abuaf, Assistant in Research, Department of Aerospace and Mechanical Sciences.

## PREVIOUS AND RELATED CONTRACTS

National Science Foundation, Grant GP-2352, 1 December 1963-30 November 1965, Grant GK-655, 1 November 1965-30 October 1967.

Office of Naval Research, Project SQUID, Contract Nonr-3623-S17-13, NR-098-038, 1 November 1963-30 September 1967.

TABLE I. Velocities and kinetic energies obtained in molecular beams from supersonic jets of carrier gas containing 1 mole percent of heavy species.

| | Helium carrier | | | | Hydrogen carrier | | | |
|---|---|---|---|---|---|---|---|---|
| Heavy Species | To (°K) | $V_{obs}$ ($10^5$ cm/sec) | $V_{obs}/V_{th}$ | $\frac{1}{2}m_h V^2$ (eV) | To (°K) | $V_{obs}$ ($10^5$ cm/sec) | $V_{obs}/V_{th}$ | $\frac{1}{2}m_h V^2$ (eV) |
| $CH_4$ | 300 | 1.70 | 0.98 | 0.24 | 300 | 2.49 | 0.95 | 0.51 |
| | 1200 | 3.47 | 1.00 | 1.00 | 900 | 4.39 | .91 | 1.59 |
| $N_2$ | 300 | 1.68 | 0.98 | 0.41 | | | | |
| | 1200 | 3.36 | .98 | 1.64 | | | | |
| Co | 300 | 1.67 | 0.97 | 0.40 | 300 | 2.40 | 0.94 | 0.83 |
| | 1200 | 3.40 | 0.99 | 1.67 | 900 | 4.18 | .89 | 2.52 |
| $C_2H_6$ | 300 | 1.69 | 0.99 | 0.44 | 300 | 2.46 | 0.97 | 0.94 |
| | 900 | 2.99 | 1.01 | 1.39 | 900 | 4.14 | .89 | 2.65 |
| $H_2S$ | 300 | 1.71 | 1.00 | 0.51 | 300 | 2.39 | 0.95 | 1.00 |
| | 1180 | 3.36 | 0.99 | 1.98 | 1070 | 4.20 | .83 | 3.10 |
| $C_3H_6$ | 300 | 1.68 | 0.99 | 0.61 | 300 | 2.21 | 0.89 | 1.06 |
| | 900 | 2.94 | 1.01 | 1.88 | 900 | 3.89 | .85 | 3.29 |
| $CO_2$ | 300 | 1.67 | 0.99 | 0.63 | 300 | 2.25 | 0.91 | 1.15 |
| | 1440 | 3.70 | 1.00 | 3.11 | 900 | 3.80 | .84 | 3.28 |
| $SO_2$ | 300 | 1.61 | 0.98 | 0.86 | 300 | 2.24 | 0.95 | 1.66 |
| | 1200 | 3.11 | .95 | 3.20 | 955 | 3.54 | .79 | 4.01 |
| $CH_3Br$ | 300 | 1.51 | 0.95 | 1.12 | 300 | 2.00 | 0.89 | 1.96 |
| | 1155 | 2.82 | .91 | 3.90 | 1155 | 3.42 | .74 | 5.75 |
| Xe | 300 | 1.40 | 0.92 | 1.33 | 300 | 1.82 | 0.86 | 2.25 |
| | | | | | 2050 | 3.25 | .53 | 7.17 |
| $SF_6$ | 300 | 1.38 | 0.91 | 1.44 | 300 | 1.77 | 0.85 | 2.37 |
| | 1150 | 2.56 | .87 | 4.95 | 1180 | 2.94 | .67 | 6.53 |

Unclassified

Security Classification

**DOCUMENT CONTROL DATA - R&D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

1 ORIGINATING ACTIVITY *(Corporate author)*

Princeton University
Princeton, New Jersey 08540

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

HIGH ENERGY MOLECULAR BEAMS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Scientific. Final. 1 Mar 1964-31 Aug 1967. Approved: 24 May 1968

5 AUTHOR(S) *(First name, middle initial, last name)*

James B. Anderson
John B. Fenn

| 6. REPORT DATE | 7a. TOTAL NO OF PAGES | 7b. NO. OF REFS |
|---|---|---|
| January 1968 | 16 | 13 |

| 8a. CONTRACT OR GRANT NO. | 9a. ORIGINATOR'S REPORT NUMBER(S) |
|---|---|
| AF19(628)-3887 | |
| b. PROJECT, TASK, WORK UNIT NOS. | |
| 4076-04, 8658-01-01 | |
| c. DOD ELEMENT | 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* |
| 62405484, 61445014 | |
| d. DOD SUBELEMENT | |
| 634076, 681310 | AFCRL-68-0189 |

10. DISTRIBUTION STATEMENT

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| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY |
|---|---|
| TECH, OTHER | Air Force Cambridge Research Laboratories (CRO)<br>L. G. Hanscom Field<br>Bedford, Massachusetts 01730 |

13. ABSTRACT

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DD FORM 1 NOV 65 1473

Unclassified

Security Classification

Unclassified

Security Classification

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| atomic beams | | | | | | |
| molecular beams | | | | | | |
| freely expanding jets | | | | | | |
| separation of species | | | | | | |
| collision processes | | | | | | |

Unclassified

Security Classification